RHYTHMIC BANDING OF MANGANESE DIOXIDE IN RHYOLITE TUFF

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The material upon which this study is based was collected by the writer on the south slope of Tumamoc Hill, the largest of a group of low hills of the same name about a mile west of Tucson, Arizona. The Desert Laboratory of the Carnegie Institution of Washington is located on the north slope of this hill. The geology of this region is presented in a paper[1] by C. F. Tolman, Jr.

As the writer had been unable to find any description of a similar occurrence of an eccentrically banded structure of manganese dioxide in rocks, it seemed to him that a description of this occurrence would be of interest. The structure will be referred to as rhythmic banding. This term seems to be the best, as the structure cannot be called an orbicular structure, which it resembles to a certain extent, because that term is applied to certain crystalline aggregates in igneous rocks.

Mode of occurrence.—The specimens of manganese dioxide were found in the talus at the foot of a bed of rhyolite tuff which outcrops on the southern slope of Tumamoc Hill. The tuff, according to Professor F. N. Guild,[2] consists of volcanic ash with numerous inclusions of pumice and darker, more basic, fragments. The volcanic ash consists of glass, fragments of quartz, feldspar, ferromagnesian minerals, and kaolinized material. Professor Guild gives the following analysis:

SiO_2	73.59
Fe_2O_3, Al_2O_3	13.95
CaO	1.41
MgO	0.75
K_2O, Na_2O	11.23

This analysis shows that the rock is very siliceous.

[1] *Publication No. 113, Carnegie Institution of Washington*, pp. 67–82.

[2] F. N. Guild, *Publication No. 113, Carnegie Institution of Washington*, p. 81, and *American Journal of Science*, XX (1905), 314.

An analysis of the material to determine the percentage of MnO_2 was made by Mrs. W. A. Tarr. It was found that it was merely a stain which was readily removed from the tuff by acids. The amount of MnO_2 present was 0.82 per cent.

At the point where the material was collected the rhyolite tuff is about 100 feet thick. It is overlain by a basalt and rests upon an andesitic conglomerate. As none of the specimens could be located on the face of the bluff it is not known whether the structure formed after the material had accumulated in the talus or while it was still in place. Likewise it cannot be determined from which part of the bed of tuff the material was derived.

Description of the rhythmically banded structure.—The light- to dark-brown color of the rhythmically banded manganese dioxide in the light-gray tuff gives the rock a very striking appearance (Fig. 1). The amount of manganese dioxide in each structure is small (see analysis above), for the tuff is merely colored and is not replaced in any way. This staining process was greatly aided by the very porous character of the material. Practically all the banded areas are circular or elliptical, the former shape predominating, though a few are irregular in outline. In size they vary from 30 mm., as a maximum, down to mere brown specks.

All the structures show either eccentric or concentric banding, this being true of those which are as small as 1 mm. in diameter. The banding is very delicate in most of them and is due to variations in the shade of the brown color. The bands are usually about a fraction of a millimeter in width, but in some of the large structures the bands are as much as 2 mm. in width, and occasionally the central zone has a diameter of 9 mm. and is uniformly tinted throughout (see Fig. 1). There are sometimes ten to fifteen bands in these larger structures. The rings are not absolutely uniform in their spacing or in their intensity, but they are so nearly so that slight variations in the composition of the solutions would account for the differences. The photographs do not show the bands clearly because of the small differences in light values between the zones. (See the drawing, Fig. 2.) The manganese dioxide affects the color of the finer pumiceous material, but as a rule does not change the color of the fragments of quartz, biotite, and other minerals

within the area of the banding. The outer part of the structures is usually darker than the interior.

The remarkable thing about these structures is that in a majority of them the bands are not concentric. In one case the nucleus was

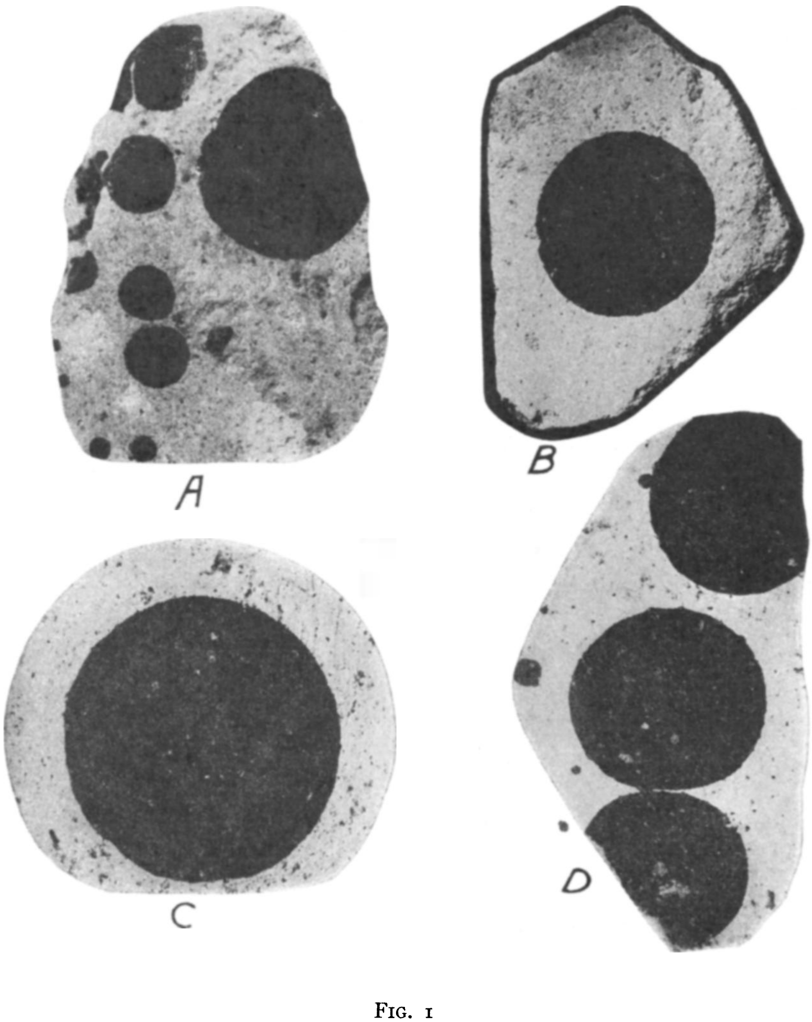

FIG. 1

A, Several spheroids in one piece of tuff
B, Spheroid showing the rings
C, Spheroid somewhat enlarged, showing rings
D, Three eccentric spheroids, slightly enlarged

8 mm. from one side and 20 mm. from the other, yet the structure was spherical. The majority have their nuclei to one side of the true center. It was this peculiar zoning that first attracted the writer's attention.

The only regularity of arrangement of the banded structures in the tuff is their relationship to the surface, as they are more numerous near the exposed surface of the fragments of tuff. All of the specimens on hand show weathered faces on one or more sides, thus indicating that the structures are definitely related to the surface of the talus blocks from which they were obtained. The largest structures are usually an inch or so from the surface, the intervening spaces being filled with numerous smaller banded areas, which not infrequently coalesce. A larger one may partially or wholly envelop a smaller one, apparently without affecting its color in any way. Again, two large ones may be so close that only a line separates them, yet each is distinct, or they may interfere and produce a lobate structure.

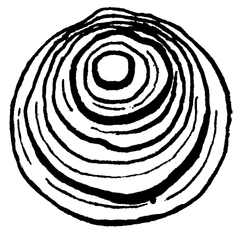

FIG. 2.—Tracing of an eccentric structure. Actual size.

A rather striking feature is the position of the nuclei in those forms that are eccentric and that lie near the weathered surface of the talus block. The nuclei are on the side of the structure which is nearest to the weathered surface, and the bands widen upon the opposite side. This may be definitely connected with the origin of the rhythmic banding. The largest structures and also those most nearly circular lie farthest below the surface. These, as a rule, are also the most perfectly banded structures.

Suggestions as to the origin of the rhythmic banding in the manganese dioxide.—The origin of the rhythmic banding is an interesting problem, and the two following suggestions appear to be the most feasible explanations of the phenomena: (1) the manganese was leached out of the tuff and deposited near the surface of the blocks, or (2) some mineral in the tuff furnished the manganese, the dioxide forming in the zone around it.

1. That the aggregation of the manganese into rhythmic zones might be due to the same process that produces the well-known

dark coating called "desert varnish," which is found on surface materials throughout the desert region appears to be plausible. This coating is thought to be due to the evaporation of water drawn from the interior by capillarity, the salts in solution being deposited at the surface. The writer has never been able to find an exact statement of the chemistry of this process, and he feels inclined to doubt the applicability of the method suggested, because iron and manganese salts are very difficult of solution even under favorable conditions, and it is well known that the arid climate of Arizona and New Mexico favors oxidation and tends to inhibit reduction, which is a necessary step in the solution of the salts of these elements.

However, in the case of the tuff the solution could circulate through it readily, as it is very porous, and if proper solvents were present some manganese might be dissolved. Upon evaporation at or near the surface, where oxidizing conditions prevail, the manganese would be thrown down as the oxide. Once started, the structure would grow by fresh additions from the outside. As the solutions were moving outward it is to be expected that the growth on the inside would be most rapid, and thus the eccentric rings would develop. Variations in the amount of manganese and the hydration of the resulting oxide would account for the color variations. At a distance from the surface the structure would be nearly circular, because of the more uniform addition of material.

It should be noted, however, that rhyolites are usually very low in manganese, which is against the theory that the manganese has been derived from the rhyolite tuff. Such rocks nevertheless occasionally contain minerals which are high in manganese, the garnet spessartite being especially common in them. Such a mineral, even though present in small amounts, when broken and scattered through a block of tuff might furnish a fair source of manganese. Likewise biotite sometimes contains manganese, and considerable biotite (nearly always hydro-biotite) occurs in the tuff. These are therefore possible sources of the manganese.

2. The manganese dioxide of the rhythmically banded structures may have originated from and developed around a fragment

of some manganese mineral. No definite evidence of the presence of such a mineral could be found, although one would be supposed to be occupying, or to have occupied, the center of the structures. The original mineral may have been spessartite, which, as has been noted, occurs in rhyolites, as at Rosita Hills, Colorado. It might also have been some manganese-rich ferromagnesian mineral, such as biotite, or one of the pyroxenes or amphiboles.

Water could readily enter the porous tuff and attack the spessartite. The manganese would be taken into solution largely by the water from the immediate rainfall and probably in the form of the carbonate. It could be carried out some distance (about one inch in the larger structures) before deposition ceased. Deposition would be caused by the oxidation of the manganese salt to manganese dioxide, a process that would be favored by the arid climate of the region.

A study of the bands favors the view that they are due to the same process as is the formation of Liesegang's rings, also known as rhythmic banding.[1] Once the manganese is in solution it will diffuse outward through the tuff. Holmes's demonstration that the rings may be produced in loosely packed flowers of sulphur shows that gels are not essential for their development. The porous tuff would be analogous to the flowers of sulphur in permitting the diffusion in this case.

The manganese solution would diffuse outward at a rate dependent upon its concentration. As it mingled with other solutions containing oxygen, the concentration of the respective ions would increase until a labile condition occurred, when precipitation would take place, thus producing a ring. The color of this ring would depend upon the concentration of the solution and in part upon the hydration of the resulting oxide. The manganese solution would then move on (provided its rate of diffusion exceeded that of the other solution) through the zone depleted of oxygen until a second

[1] Recent discussions of rhythmic banding or precipitation are given in the following papers: J. Stansfield, "Retarded Diffusion and Rhythmic Precipitation," *Am. Jour. Sci.*, 4th series, XLIII (1917), 1–26; H. N. Holmes, "Rhythmic Banding," *Science*, New Series, XLVI (1917), 442; J. Stansfield, "Rhythmic Precipitation," *ibid.*, New Series, XLVII (1918), 70.

concentration occurred. As the solutions became weaker the rings would become farther and farther apart unless the concentration of the oxidizing solution became stronger. The width of the zones between the rings would depend upon the relative rates of diffusion of each solution. That there was a slight change in the concentration of the solution as long as there was a source of the manganese is shown by the gradually increasing intensity in color in the outer portions of the structures. The larger fragments of minerals in the tuff are uncolored because of their density.

The eccentric character of the banding is probably the result of several factors. The rate of diffusion of the two solutions was probably different in different directions. The rate of diffusion inward from the surface of the oxidizing solution was probably most rapid, hence the oxidizing solutions met the manganese solutions nearer the nucleus on the side nearest the surface. This interpretation is in accord with the fact that the majority of the structures show wider zones of rings on the side opposite to the surface, where the rate of diffusion of the manganese solutions is greater than that of the oxidizing solutions. Another factor may have been the varying porosity of the tuff, although this is not so likely as the foregoing, because it is not probable that the majority of the banded structures should have the same variation in porosity on the same side. When the blocks of tuff were lying in the proper position downward diffusion as influenced by gravity might aid in producing the eccentric rings. Unlike in laboratory experiments, where the rhythmic banding is produced in a gelatine of uniform composition and density, the rhythmic banding in nature would find varying factors on all sides, hence one should really expect the banded structures to vary from perfect rings. The varying width of the rings themselves is due to the variable character of the solutions. It would seem that this suggestion as to the origin is the better of the two and, if correct, furnishes an interesting example of rhythmic banding in rocks.

Summary.—Rhythmically banded structures of manganese dioxide are found in rhyolite tuff near Tucson, Arizona. These structures are eccentric, which is an unusual mode of occurrence.

They are apparently due either to the manganese being derived from the surrounding tuff and aggregated into the banded forms, precipitation being due to oxidation, or to the mangagese dioxide being derived from a mineral located at the nucleus of the structure and being precipitated in successive rings by rhythmic precipitation following the mingling of the outwardly moving manganese solution with one of oxidizing character. The latter view is believed to be the most probable.